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Preview

Bright and Blue Nanocrystal Emitters

Brandon R. Sutherland^{1,*}

The discovery and development of blue light emitting diodes (LEDs) enabled energy-efficient white light emission that continues to impact global energy consumption today. Alternative materials that can outcompete commercial blue LEDs based on epitaxial InGaN could have a large impact on the lighting industry and in curbing anthropogenic climate change. Recently in *Joule*, Congreve and colleagues show that metal halide perovskite nanocrystals—greatly improved by Mn incorporation—have promise for low-cost, efficient, and bright blue LEDs.

One of the largest uses of energy goes toward lighting. In 2017, the U.S. used approximately 7% of its total electricity consumption for lighting the residential and commercial sectors.¹ The adoption of energy-efficient lighting solutions can have a large impact on global energy use and plays an important role in reducing greenhouse gas emissions that drive anthropogenic climate change.² Technologically mature lighting solutions are based on incandescent and fluorescent light bulbs. Light-emitting diodes (LEDs) are an energy-efficient lightning technology projected by the U.S. Department of Energy to save over 5 quadrillion British thermal units (BTUs) annually by 2035.

This is equivalent to about the total annual energy consumption of 45 million U.S. homes today and is a 75% reduction in energy use compared to relying on incandescent and fluorescent lighting.³ LEDs are already galvanizing the landscape of residential and commercial lighting and have further enabled many of the great technological advances of the electronic display industry.⁴ LEDs are the standard for energy-efficient screens in mobile devices, televisions, and monitors.

An important aspect of LEDs is that they can be tuned to emit light at different wavelengths, depending on the material used. By the early 1970s, LEDs that emit

at wavelengths ranging from red to green had been demonstrated.⁵ The development of a blue LED was significantly more challenging. Blue light emits at approximately 470 nm on the electromagnetic spectrum, corresponding to an energy of about 2.6 eV. To achieve blue emission, a high-quality semiconductor with a band-gap energy of about 2.6 eV is required. Further, materials with the right energetic band alignment that can efficiently inject carriers into the emissive layer are needed. It was not until 1994 that Shuji Nakamura and colleagues at the Nichia Corporation were able to realize this by forming a compositional blend of InGaN with the right band gap, and they developed a double-heterostructure with AlGaIn to effectively confine carriers in the emitting layer, enabling a blue LED with an external quantum efficiency of 2.7%.⁶ For this and prior work in this area, Nakamura and collaborators were awarded the 2014 Nobel prize in physics.

Blue LEDs were a big challenge to make, but their importance cannot be understated. The development of

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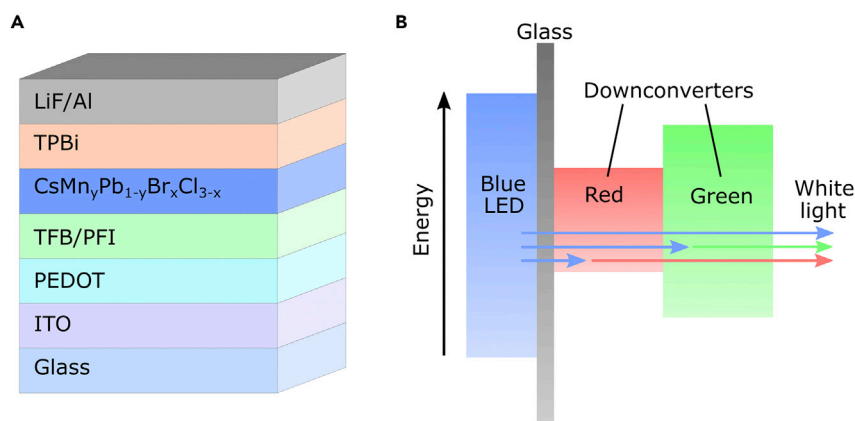


Figure 1. All-Perovskite White LED

(A) Blue Mn-doped perovskite LED architecture. Acronyms for each layer are defined in Hou et al.⁷
 (B) Blue perovskite LED with red and green perovskite downconverters, emitting white light.

blue LEDs completed the visible spectrum of emitting wavelengths, enabling the development of white LEDs. White light comprises a mixture of light of different wavelengths. There are two common ways to generate white light from an LED. First, the emission of red, green, and blue LEDs can be spatially combined to form white light. Second, some of the emission from a blue LED can be harvested by red- and green-emitting phosphors and re-emitted in the right ratios to generate white light. In both cases, a blue LED is required. Today, most commercial blue LEDs are still made from InGaN heterostructures. Alternatives such as AlGaIn/GaN, SiC, or ZnTe/ZnSe nanocrystals each have their own challenges and disadvantages. Continued research and development into new alternative materials for bright, energy-efficient, and stable blue LEDs is needed.

Recently in *Joule*, Congreve and colleagues demonstrate a blue LED made from metal halide perovskite nanocrystals with enhanced efficiency and brightness by incorporating manganese to the crystal lattice.⁷ Metal halide perovskite nanocrystals are an emerging material with many attractive properties for light emission, including sharp luminescence linewidths, high

photoluminescence quantum yield, and color tunability throughout the visible spectrum.⁸ Unlike compound semiconductors used in commercial blue LEDs, these materials can be fabricated at low temperature from printable semiconductor inks. Here, the authors show that incorporating Mn into the lattice of CsPbBr_xCl_{3-x} greatly improves its optical properties. They show evidence that Mn dopants passivate defects in the nanocrystal, suppressing nonradiative recombination.

The CsMn_yPb_{1-y}Br_xCl_{3-x} perovskite shows a 4-fold improvement in external quantum efficiency (EQE) relative to the Mn-free control when used as the active layer in a blue LED (Figure 1A). The peak EQE of 2.12% at 466 nm is the highest reported for perovskite emitters that meet the National Television System Committee (NTSC) spectral standard for blue light to date. The device shows a maximum brightness of 245 cd/m² and an emission linewidth of 17.9 nm, both improved through Mn doping. The authors further demonstrate their blue LED in a proof-of-concept all-perovskite white light LED using red and green perovskite downconverters (Figure 1B). The red perovskite layer downconverts the higher energy blue photons, re-emitting them

at red wavelengths. The final green perovskite layer absorbs the blue photons that were not absorbed by the red layer, re-emitting them at green wavelengths. The combination of red, green, and blue gives white light, which the authors show is near the ideal white light spectrum.

The topic of energy efficiency is well represented by energy funding agencies, such as the U.S. Department of Energy, and is often an area where some of the largest returns on investments have been realized.⁹ The continued progress and development of metal halide perovskites in blue emission is an important area of material science and photonics research and an exciting emerging technology for energy-efficient lighting. Future challenges will be to not only increase the efficiency of these devices, but—equally important—stabilize them for long-term operation to reduce the levelized cost of energy for lighting solutions over the span of their lifetime. Current state-of-the-art perovskite LEDs typically degrade within minutes without encapsulation. Evaluating degradation mechanisms at early stages of development is a critical consideration for any emerging functional material to improve its chances for applications at scale in the future.¹⁰

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Preview

The Many Shapes of Lithium

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Lithium metal is known to form ramified structures during electrodeposition not only at high current densities (above diffusion limit) but also, unexpectedly, at low currents. In this issue of *Joule*, Bai and coworkers describe an analytical approach to explain structural evolution of lithium electrode at different current densities. They find three distinct regimes as a function of current rate, such that the morphology changes from whiskers to mossy to dendrites.

Metal electrodeposition is a well-studied and matured area of engineering. However current phenomenological observations related to instabilities in electrodeposition of reactive metals like lithium and sodium pose new questions and challenges. Perhaps the greatest opportunities in understanding and finding fundamental solutions for these instabilities is in the context of energy storage. As the demand for high-capacity and long-lasting energy storage devices increases, lithium-metal batteries (LMB) that use metallic lithium as anode can be a suitable replacement for lithium-ion batteries, resulting in an increase in energy density by at least five times.¹ A major hurdle in adapting a LMB is its tendency to fail by rampant short circuits due to formation of ramified structures during electrodeposition, termed “dendrites.” In the absence of any convection, dendritic growth in metal electrodeposition is known to happen only by diffusion limitation when the operating current exceeds the rate of cation diffusion. However, LMBs have been widely reported to fail by short circuit even when operated at lower currents. These

observations are critical due to their implication in determining the current limits for safe battery operation. What makes lithium-metal electrodeposition challenging is its tendency to react with the electrolyte to form a passivating layer commonly known as SEI (solid electrolyte interphase). An uncontrolled rate of reaction between the metal electrode and electrolyte can lead to divergence of interfacial resistance, thus causing rapid battery capacity fade. Also, the spatial heterogeneity of the SEI layer drives morphological heterogeneity during electrodeposition. It has been seen that the interfacial chemistry plays an important role in the morphological stability of electrodeposition, which can’t be explained by only considering the transport characteristics of the charge-carrying ions and dielectric media.

In this month’s issue of *Joule*, Bai et al. report a novel analytical approach to explain the structure and growth mechanisms of dendrites during electrodeposition of reactive metals.² The work discusses three distinct regimes of electrodeposition depending on the cur-

rent density of operation (Figure 1). (1) At low current densities, the growth mechanism is described as “root-growth,” resulting in human-hair-like structures (whiskers). As lithium can react with the electrolyte even in the absence of an electric field, the SEI is present irrespective of the current density. If the rate of deposition is under a critical value (J_{cc}), then the SEI remains intact and the deposition happens under the SEI. However, with prolonged deposition times, internal stress under the SEI builds up, which often results in the release of pressure in the form of whiskers through the weak points (or pinholes) in the SEI layer. Further deposition under the SEI layer causes the whiskers to be pushed out in the form of wires. (2) At very high current densities, beyond the limiting rate (J_{lim}), a space-charge region is formed on the electrode surface due to anion depletion, resulting in diffusion-limited dendritic growth by a tip-growth mechanism forming tree-like fractal structures. This phenomenon is well understood irrespective of the nature of SEI. (3) Bai et al. further illustrate a third regime of electrodeposition at an intermediate rate ($J_{cc} < J < J_{lim}$).² This regime is fundamentally important because it is associated with a widely observed yet relatively less understood “moss-like” deposition, and it is also in the desired operating range for fast-charging LMBs ($\sim 0.7J_{lim}$). At these

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